

# **Report for 2001ID4501B: Factors Controlling the Availability of Phosphorous for Transport into Surface Waters from Manure Amended Soils in Southern Idaho**

- Conference Proceedings:
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  - Western Soil Science Society Meetings, Moscow, 2001
  - Washington State Professional Soil Science Society Meetings, Pullman, WA 2001
  - Pacific Northwest Water Quality Meetings, Vacouver, WA, 2002.
  - Idaho Nutrient Management Conference, Twin Falls, 2002.

Report Follows:

### **Problem and Research Objectives:**

Over the past decade the dairy farm industry in Southern Idaho has experienced significant growth. Between 1990 and 1999 there has been an 85% increase in milk production. Intensive dairy and livestock operations require adequate land base for disposal of manure produced during operation. Often it is not economically feasible to haul manure long distances to broaden the land used for disposal. This has caused concern over the disposal of animal wastes generated. A primary concern is loss of phosphorus to surface water which leads to eutrophication and a decrease in water quality.

The P-cycle in soils is a dynamic system involving soil, plants, and microorganisms. Major processes include uptake of solution P by plants, recycling through return of plant and animal residues, biological turn over through mineralization-immobilization, fixation reactions at clay and oxide surfaces, and solubilization and formation of mineral phosphates through chemical reactions and activities of microorganisms (Stevenson et al., 1986).

Although a P-index and P-threshold limits have been set, there is little known about the cycling of P in So. Idaho Soils. The P-threshold established by the Idaho Dairy Nutrient Management plan does not consider true P reaction processes that affect its release behavior in So. Idaho Soils. The goal of this study is to investigate the biogeochemistry of P cycling in soils. In specific, we hypothesize that organic and inorganic P have unique reaction behaviors in soils, and that the availability of the compounds is dependent on reaction processes. To test this hypothesis the following objectives have been developed. First to measure desorption kinetics of P from manure amended soils. Then to speciate P in manure amended soils and leachate. These objectives are designed to investigate organic and inorganic P reaction behavior in soils in order to gain a better predictive understanding of the fate of both inorganic and organic P in soils.

### **Methodology:**

Desorption kinetics were measured from agricultural soils in So. Idaho located in Gooding County. These soils are classified as a deep, well drained, fine sandy loam (Kecko series). The primary use of these soils is for cropland, pasture, hayland, and in this case for the disposal of dairy wastes. At the time of sampling the crop being grown was corn. Samples were taken from a dairy farm. Three random surface (0-10 cm) samples, and subsurface (45 cm) samples were taken from both the north and south fields. The south field receives applications of lagoon liquid animal wastes through sprinkler-irrigation throughout the growing season. The north field receives solid animal wastes applications primarily in the spring prior to planting.

To measure the desorption kinetics and speciation of P from manure amended soils we used a batch technique. This was done by mixing 2 grams of soil with 40 ml of 0.01 M  $\text{CaCl}_2$  or 0.005M  $\text{NaCl}_2$ . The  $\text{CaCl}_2$  extractant was used to simulate soil water in calcareous soils, while the  $\text{NaCl}_2$  extractant was used to simulate P availability from low ionic strength water (irrigation or rain water). The samples were then placed on an end over end shaker for time intervals ranging from 30 minutes to 21 days and allowed to equilibrate. The pH of the samples was monitored throughout the experiment. The initial pH of the north surface, north subsurface, south surface, and south subsurface was 8.4, 7.7, 8.4, and 8.6 respectively. Throughout the experiment there was little or no variance in pH. At each time interval the samples were centrifuged and filtered through a 0.2  $\mu\text{m}$  filter membrane. The samples were analyzed for inorganic P using the molybdate blue method on a Lachat instrument, and a modified molybdate blue method on the spectrometer. The modified molybdate blue method is used to prevent the hydrolysis of organic P. The same samples were then analyzed on the ICP for total P. Organic P can then be

calculated by taking the difference between the ortho-P determined by the molybdate blue, and the total P determined by the ICP.

An Olsen-P (0.5 M NaHCO<sub>3</sub>) test was also conducted on the samples. As well as a microwave digestion procedure to determine total P in the soils. These samples were analyzed on the ICP to determine extractable P and total P.

Abiotic experiments were conducted by sterilizing soils, desorption solutions and incubation tubes in an autoclave. Abiotic integrity of the solutions was verified by plating the samples at the end of the incubation on bacteria and fungi growth media.

### **Principal Findings and Significance:**

Initially an experiment was conducted to test the sensitivity of the Lachat and the ICP for distinction between organic and inorganic P. Inorganic P (Ortho) as well as four other organic P compounds were analyzed on the Lachat and ICP. The results (Table 1) show that inorganic P was recovered on both the Lachat and ICP, and the organic P was recovered only on the ICP.

The digest of the soils resulted 900-1000 mg/kg P for the surface soils and 600-700 mg/kg P in the subsurface soils. The Olsen-P results for the surface samples yield 9 mg/L and 2-3 mg/L for the subsurface samples. For the surface samples 19-20% of the total is recovered by the Olsen-P test, and in the subsurface samples only 7-8 % of the total is recovered by the Olsen-P test. The results are given in Table 2.

The desorption of P in the surface and subsurface samples for both the North and South fields are characterized by sharp initial increase in the P desorbed followed by a leveling off in P concentrations. The results from the Lachat, spectrometer, and the ICP gave the same concentration of P (Figure 1). This suggests that there is no soluble organic P being desorbed into solution. Results from NMR analysis on the soil extracts confirm that the soluble P phase consists of nearly 100% ortho phosphate.

Desorption of P in the surface soils takes up to 300 hours to reach the maximum concentration (7 mg/L), i.e., equilibrium is reached between 10-12 days (Figure 2). After 24 hours 80% of the leachable P has been desorbed, indicating that P desorption is slow and can continue for up to 21 days with only 15% of the total P being desorbed.

Desorption kinetic results from the subsurface soils are similar to the surface samples; they take up to 300 hours to reach maximum desorption (1.5 and 0.5 mg/L) with 80% of the P being desorbed after 24 hours. Desorption of P in the subsurface samples only recovers 2.77 and 2.1 % of the total P. The South subsurface soil had 2.5 times as much total P as the North subsurface soil. This increased loading in the subsurface soil indicates that the soluble P is being transported lower than it is in the North field. The application of P via irrigation using lagoon water is likely the reason for the increased P leaching.

The desorption kinetics of Ca, Mg, and Si were also measured. The release of these elements parallels P desorption (Figure 4). Calcium and magnesium can form poorly soluble apatite-type minerals controlling the release of P, and soluble Si is present in soils as an oxyanion with similar desorption characteristics as phosphate.

Desorption curves using NaCl<sub>2</sub> and CaCl<sub>2</sub> as the background electrolyte had similar trends (Figure 5), however, the NaCl extractant resulted in almost twice the concentration of desorbed P compared to the CaCl<sub>2</sub> extractant. The reason for this may be that calcium in solution inhibits the desorption/dissolution of additional calcium from Ca-P minerals. In addition, any P that does desorb can form Ca-P mineral precipitates and fall out of solution.

Abiotic kinetic experiments were conducted to measure the impact of microbial activity

on P release curves. Results indicated that microbial activity had little impact on the P desorption behavior suggesting that the controlling reaction for P desorption is desorption or dissolution of P containing minerals.

Investigation of the soil P speciation using NMR on NaOH/EDTA extracts suggests that up to 20% of the P in the soils is present as an organic molecule. The stability of this fraction is unknown, however, our results clearly indicate it is not soluble as an organic P molecule. Upon hydrolysis the organic P may desorb into solution as inorganic orthophosphate, or be taken up by soil minerals. If this phase hydrolyzes and then desorbs it would represent a large flux of soluble P that may enter the surface or ground water. Future experiments will be carried out to investigate the stability of such organic P molecules with soil minerals.

### Summary

Phosphorus desorption is characterized by a curve in which there is a fast initial increase in the desorbed P followed by a slow secondary reaction that can continue for up to 21 days. In all cases it took up to 300 hours for desorption to reach a maximum. The amount of desorbed P is only 10-15 % of the total P in the soil.

With a better predictive understanding of the geochemical cycling of phosphorus in manure amended soils, one could give better recommendations for the use of these animal wastes as soil amendments. As a result surface water pollution will be decreased, waste disposal will be optimized, and the dairy industry will be sustainable.

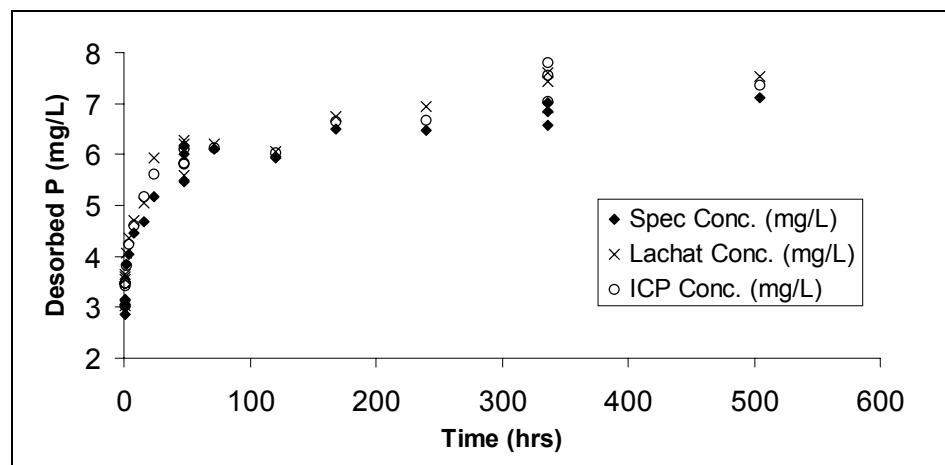
**Table 1.** Sensitivity of Lachat and ICP for organic P.

Sample	Lachat Conc. (ppm)	ICP Conc. (ppm)
Ortho-P (0.5 ppm)	0.51	0.49
Phytic Acid (0.5 ppm)	0	0.47
Glycerol Phosphate (0.5 ppm)	0	0.45
Sodium Pyrophosphate (0.5 ppm)	0	0.43
Phenolphthalein Diphosphate (0.5 ppm)	0	0.44

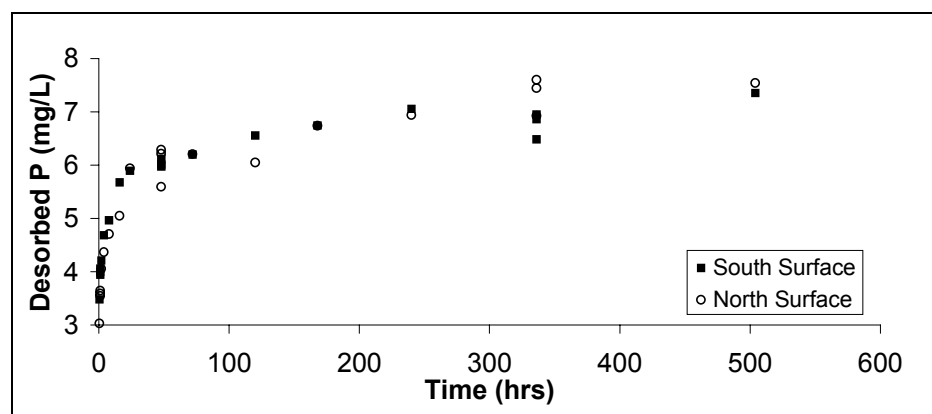
**Table 2.** pH and P content of soils.

Soil Properties	North Surface	North Subsurface	South Surface	South Subsurface
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pH	8.4	7.7	8.4	8.6
Total P (mg/kg)	9	600	1000	700
Olsen-P (mg/L)	9.19	2.14	9.44	2.77
Percent total Olsen P extracted	20.4	7.13	18.9	7.9



**Figure 1.** Desorption kinetics from the North field soil showing readings from the three methods of detection



**Figure 2.** Desorption kinetics of P from the surface soils.

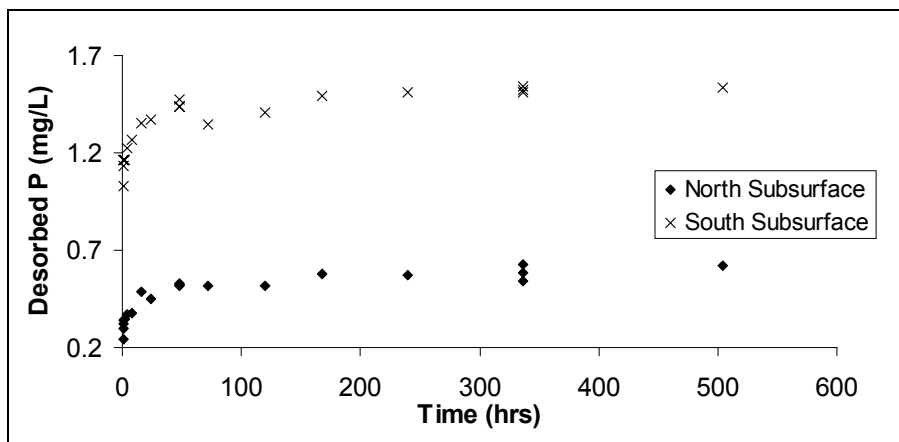


Figure 3. Desorption kinetics of P from the subsurface soils.

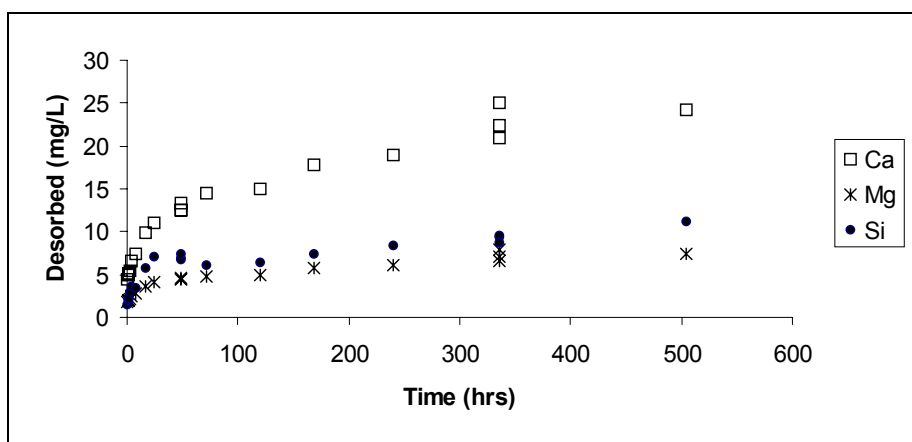


Figure 4. Desorption kinetics of Ca, Mg, and Si from the North surface soil.

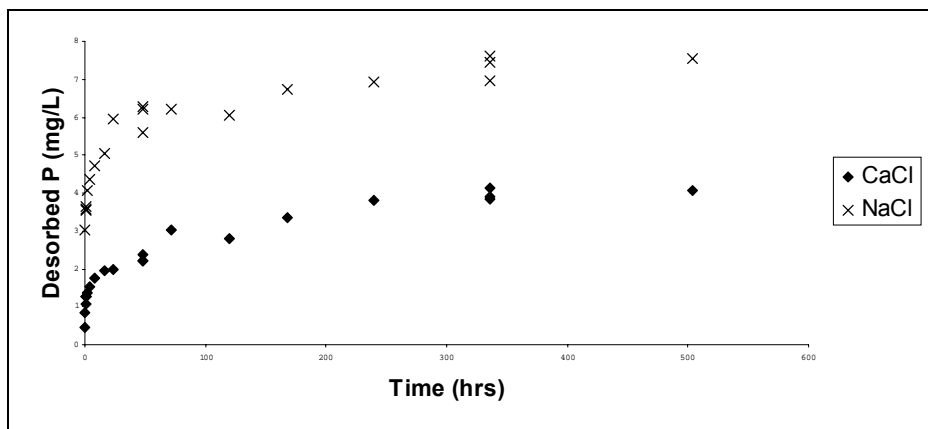


Figure 5. Comparison of P release from the North surface soil using CaCl<sub>2</sub> and NaCl.